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Short communication

First coordination polymers on the bases of chiral thiophosphorylated thioureas

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ABSTRACT

The preparation and structure of the new coordination polymers $[NiL_2pz]_n$ (HL = (*rac*)-, (*R*)- or (*S*)-$PhCH(CH_3)NHC(S)NHP(S)(OEt)_2$) were described. The preliminary biological test revealed high activity of the complexes towards *Staphilococcus aureus* and *Bacillus cereus*.

Thiophosphorylated thioureas attracted considerable attention in the last few years [1]. This interest is explained by the availability of such thioureas [2], their anti-microbial activity [3] and structural diversity of their complexes with transition metal ions [4]. To the best of our knowledge, no biological activity data were reported for the complexes of the thiophosphorylated thioureas, although for the complexes of acylthioureas the biological activity is even higher than for individual ligands [5]. The same effect can be expected for the complexes of thiophosphorylated thioureas.

Even more important factor related to biological activity is enantiomerism. However, chiral thiophosphorylated thioureas and their complexes, both in racemic and enantiopure forms, have not so far been investigated. In our opinion, the insertion of chiral fragments into thiophosphorylated thioureas will offer new prospect for the development of compounds exhibiting biological activity.

Herein, we report the synthesis of chiral thiophosphorylated thioureas and their Ni(II) complexes, their structure and some properties.

New chiral thiophosphorylated thioureas were synthesized by the addition reaction of commercially available 1-phenylethylamine in racemic and enantiopure forms with *O,O*-diethyl thiophosphoryl isothiocyanate (Scheme 1). This reaction proceeds at room temperature in benzene in inert atmosphere resulting in the formation of (*rac*)-, (*R*)- and (*S*)-1-(1-phenyl)ethyl-3-(*O,O*-diethylthiophosphoryl)thioureas. According to ^{31}P NMR spectra of crude reaction mixture there are no byproducts detected in this reaction. Analytically pure thiophosphorylated thioureas can be obtained by crystallization from cyclohexane in good yield.

The obtained ligands were further used to attain Ni(II) complexes. The complexation reactions of thioureas with transition metal salts are generally carried out in the presence of a proton acceptor, providing the deprotonation of the ligand, followed by the addition of the metal cation. The base is usually not included into the metal coordination sphere [6]. In the reaction of chiral thioureas **HL** with nickel acetate (II), we have used a different approach which involves pyrazine as a base. Being able to form coordination bonds with Ni(II) ions, pyrazine may serve as an aromatic bridge between the metal ions. The complexation reaction (Scheme 2) gave a coordination Ni(II) polymer for both racemic and enantiopure ligands.

Surprising enough, the structural data on 1D polymeric chains with transition metal ions bound *via* pyrazine are scarce [7]. The only 1D structure containing thiourea ligands consists of Ni-pz-chains, with each nickel ion being also bound by achiral phosphorylated thioureas [8]. Moreover, the authors note that the formation of a coordination polymer is accompanied by a change in the coordination mode of ligand from 1,3-*N,S*, characteristic for the $[NiL_2]$ mononuclear complexes, obtained using *N*-monosubstituted phosphorylated thioureas [9], to *cis*-1,5-*N,O*-coordination.

X-ray single diffraction study revealed the formation of the 1D polymeric structure with the ratio of ligand:metal:pyrazine being equal 2:1:1 for both racemic (**1**) [10] and enantiopure (**2**) [11] crystals

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